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Viscometric determination of dialdehyde content in periodate oxycellulose Part II. Topochemistry of oxidation

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Abstract

The kinetics of periodate oxidation of cellulose was followed through the alkaline degradation of the dialdehyde groups by measuring the viscometric degree of polymerisation and the alkali consumption. The obtained results show that a fast but limited attack of periodate occurs in the amorphous region of cellulose, causing the decrease of degree of polymerisation to its levelling-off value. The alkali consumption indicates at least two further slower reactions, that lead to the asymptotic complete oxidation of cellulose units. With the pseudo first-order approximation, the oxidation half-time of these three reactions can be calculated, corresponding to 1.2, 20 and 854 h respectively. In spite of the high oxidation of the analysed samples (up to about 46%), the residue after alkaline degradation shows a relatively high value of degree of polymerisation rather than the narrow molecular weight distribution of oligomers expected from a random oxidation, thus indicating that periodate oxidises cellulose in isolated domains. The sequence of analyses over the same sample utilised in this work (titrimetry, weight loss and viscometry), performed at room temperature in mild conditions, makes it possible to investigate the topochemistry of oxidation of paper and textiles of historic and artistic value with microdistructive techniques on a single, very small fragment of material.

Abbreviations: α – fractional weight loss; DAU – dialdehyde units; DP – viscosity average degree of polymerisation (with suffixes ac – acidity degraded samples; hmw – high molecular weight fraction; lmw – low molecular weight fraction; ox – oxidised samples; oxred – oxidised and reduced samples); S – number of *β-alkoxy scissions;* $t^{0.5}$ – oxidation half-time

Introduction

Chemical modifications of cellulose give rise to a variety of derivatives of great industrial importance. Among these, the 2,3 dialdehyde cellulose obtained by periodate oxidation in a specific way under mild and easily controlled conditions can be utilised either as precursor for more complex compounds (Casu et al. 1985; Rahn and Heinze 1998) or as such for specific uses (Mašura 1974;

Kim and Kuga 2000; Kim et al. 2004). The latter aspect can be fruitfully exploited in the field of paper conservation science in order to obtain some specifically-oxidised standards useful to investigate the presence and reactivity of oxidised units in the cellulose-based historic materials (Whitmore and Bogaard 1994, 1995; Princi et al. 2004). The synergism between oxidation and acidity greatly increases the rate of degradation (Margutti et al. 2001) of these materials, and it might be important to evaluate both the amount and the position of oxidised units along the cellulose chains with some simple and microdestructive techniques, at least as a screening of the authentic specimens before performing more complex analyses (Potthast et al. 2003). In a previous paper (Calvini et al. 2004) it has been shown that the β-alkoxy mechanism of fragmentation of periodate oxycellulose in alkaline medium allows to evaluate the amount of carbonyl groups by comparing the viscometric degrees of polymerisation before and after the reduction of oxidised groups. However, the viscometric technique detects only the oxidised groups randomly displaced along the chains, while it is insensitive to the overall content of dialdehyde groups. Some WAXS and FTIR preliminary analyses (Calvini et al. 2006) confirmed that a non-uniform extensive cluster attack occurs during the oxidation (Sihtola 1960; Kim et al. 2000), at the expense of crystallinity. The aim of this paper is to evaluate the topology of the reaction by comparing the results of the viscometric technique with those obtained from titrimetric analyses at low and intermediate levels of periodate oxidation.

Materials and methods

Materials

All the chemicals utilised were analytical-grade commercial products. The source of cellulose was Whatman no. 1 filter paper, chromatographic grade. To avoid the possible influence of already existing oxidised groups, the paper was purified by 1 day immersion in 0.1 M NaOH, followed by washing and 1 day immersion in 0.1 M HCl. The withdrawn sample was then washed with distilled water to the neutrality and showed (Calvini et al. 2006) a levelling-off DP of 195 and a X-ray crystallinity of 88%.

Periodate oxidation

Paper samples were immersed for 1, 24, 48, 120 and 264 h in 0.1 M sodium metaperiodate (pH 4.25) in the dark at room temperature, at a consistency of 1 g/100 ml (ratio NaIO4/glucopyranose = 1.62). The final pH's were 4.20, 4.10, 4.08, 3.94 and 3.68 respectively. After extensive washing with distilled water and drying at room temperature and humidity, the recovered samples showed a negligible weight loss.

Titrimetric analysis

About 0.03–0.1 g of periodate oxycellulose (depending on the degree of oxidation) were immersed in exactly 10 ml of 0.01 M NaOH and left to react at room temperature. After the required time (1–2 h), 10 ml of 0.01 M HCl were added to the alkaline medium and the NaOH consumption was back-titrated with 0.01 M NaOH. During the permanency of the oxidised samples in the alkaline medium, the aqueous phase showed an increasing yellowish colour and a slight opalescence. At the end of each analysis, the cellulose suspensions were filtered on a weighted sintered glass filter (Gooch G2) in order to evaluate the weight loss.

Oxime formation

About 100 mg of periodate oxidised samples were immersed in 100 ml solution of 0.2 M hydroxylamine hydrochloride in a pH 4.4 0.1 M acetate buffer (ratio hydroxylamine/glucopyranose = 32.4) and stirred 48 h at room temperature. The recovered product was washed with deionised water, filtered and dried 24 h at 80 °C. The nitrogen content of the obtained oximes was determined by EA 110 CHNS-O gas chromatographer.

Reduction of oxidised groups

The reduction was performed by 24 h immersion of periodate oxidised samples in 0.2 M solution of tert-butylamine borane (Bicchieri et al. 1999) in 0.2 M phosphate buffer (pH 7) at a consistency of 1 g of paper/100 ml. After washing, the samples were allowed to dry at room temperature and showed a weight loss of 3, 5, 7, 27 and 36% respectively. The completeness of the reaction was verified by the absence of NaOH consumption as well as by FTIR analysis (Calvini et al. 2005).

Degree of polymerisation (DP)

The viscosity-average DP was measured at 25 °C, according to the ASTM Standard D 1795–90.

Results

In order to simplify the discussion of the experimental results, Figure 1 shows the mechanism of the alkaline β-alkoxy degradation of a *n*-cluster fragment of periodate oxycellulose, where compounds (I) and (III) belong to the high molecular weight residue, while compound (II) represents the low molecular weight soluble fraction. The hemiacetal alkoxy anions (II) and (III) quickly hydrolyse in mild alkaline medium at room temperature (Calvini et al. 2006), and prolonged treatments with alkali further hydrolyse all the oxidised groups (I–III) yielding, ultimately, glycolic and α γ-dihydroxybutyric acids by Cannizzaro's rearrangement, together with volatile acids and other non-volatile neutral/acidic fragments (O'Meara and Richards 1958).

Broadly speaking, the NaOH consumption gives the sum of compounds (II) and (III), while the viscometric analysis gives the average amount of long-chain residues (I and III). Owing to the bimodal distribution of high- (I, III) and low-molecular weight compounds (II), the viscometric analysis should be performed (Calvini 2005) on the insoluble residue (I and III), in order to evaluate the extent of side scissions that led to the decrease of degree of polymerisation without the interference of the small fragments (II).

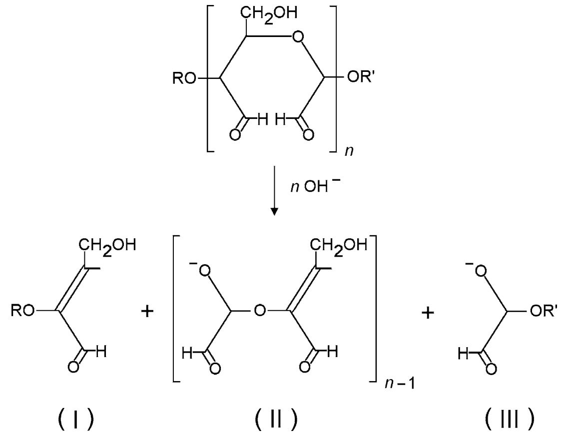

Figure 1. Mechanism of β-alkoxy fragmentation of n-neighbour oxidised units of periodate oxycellulose. H atoms, not involved in the reaction, are not shown for clarity.

Viscometric analysis

As shown in our previous work (Calvini et al. 2004), the decrease of viscometric DP after oxidation (DPox) is due to the sum of β-alkoxy scissions (induced by the alkalinity of cupriethylenediamine) plus some hydrolytic scissions (induced by the acidity of periodate), so that the overall side scissions (randomly displaced along the chains) in mmol/100 g are given by

$$\mathrm{Sside} = 617\times(2/\mathrm{DPox} - 2/\mathrm{DP}^\circ) \qquad (1)$$

where DP° is the viscosity-average degree of polymerisation of the never oxidised sample.

Nevertheless, the amount of side scissions calculated from Equation 1 deviates from a first order kinetics at long reaction times, as shown in Figure 2 (squares). Taking into account that the viscometric method requires a β-alkoxy fragmentation performed directly in the viscometer, it is likely that this deviation is due to the progressive

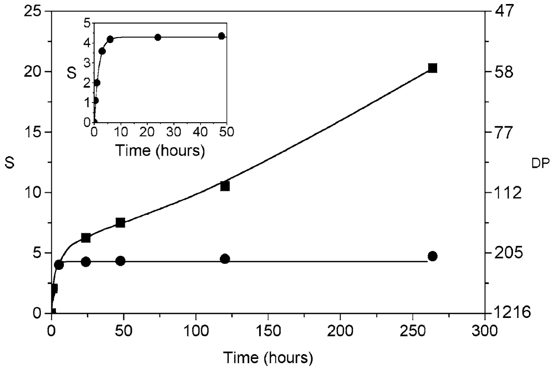

Figure 2. Number of β-alkoxy scissions (S, mmol/100 g) of periodate oxycellulose as calculated from the viscometric degree of polymerisation (DP). Squares: analysis performed directly on the oxidised samples (the line is only a guide for the eyes). Circles: re-elaboration of the same data corrected taking into account the weight loss (the line represents the best fit with a first-order rate equation, enlarged in the inset).

accumulation of the resulting low molecular weight fragments of degradation (II in Figure 1), that gave rise to a bimodal distribution. In order to evaluate the amount of scissile units randomly displaced along the chains without the interference of the oxidised clusters, the low molecular weight fragments should be removed (Calvini 2005) by intentionally causing the β-alkoxy fragmentation in heterogeneous alkaline medium before performing the viscometric analysis of the insoluble residue. An alternative method is to exploit the alkalinity of the cupriethylenediamine and to correct the experimental DPox values of the untreated oxidised samples (squares in Figure 2) taking into account the weight loss (determined as above in a separate experiment) through the relationship:

$$\mathrm{DPox} = (1-\alpha)\mathrm{DPhmw} + \alpha\mathrm{DPlmw} \qquad (2)$$

where α is the fractional weight loss and the suffixes hmw and lmw indicate the high- and low-molecular weight fragments respectively. Equation 2 can be easily demonstrated by considering the first- and second-order moments of a distribution (Herdan 1953), and its applicability to the viscometric analysis was tested by comparing the calculated and the observed values in mixtures of cellulose, hydrocellulose and cellobiose.

A comparison between the results of both the above methods showed that the application of Equation 2 to the DP of the periodate oxidised samples gives more reproducible results than the viscometric analysis of the insoluble residue after alkaline removal of low molecular weight fragments. It was observed that the latter method gave more scattered results if performed with badly washed samples after a long time lag, possibly owing to the instability of periodate oxycellulose in alkaline medium. In fact, the NaOH treatment might cause some alkaline hydrolysis, other than the β-alkoxy fragmentation, and it should be taken into account that only 1 further average scission per cellulose chain already causes a 50% drop in the value of DP.

Table 1 and Figure 2 (circles) show that the amount of side scissions, calculated from DPhmw (i.e., corrected by the weight loss), follows a first-order kinetics $\mathrm{Sside} = n^\circ(1 - e^{-kt})$ with $k = 0.6\ \mathrm{h}^{-1}$ (oxidation half-time $t^{0.5} = 1.2$ h) and an asymptotic value $n^\circ = 4.3$ mmol/100 g (corresponding to about 0.7 dialdehyde groups per 100 anhydroglucose units), with a slight drift of the last 2 points, due to the shortening of the crystallite size already detected from WAXS analysis (Calvini et al. 2006) and enhanced by the hyperbolic relationship between the number of scissions and DP (Calvini 2005).

Determination of carbonyl groups

Hofreiter et al. (1955) proposed a rapid estimation of carbonyl groups in oxycellulose by means of titrimetric analysis of alkali consumption during the β-alkoxy degradation. In their method the oxidised samples were degraded in NaOH at about 70 °C for exactly 1 min to minimise the occurrence of secondary reactions that resulted in an overestimation of the dialdehyde groups content. Owing to the variety of reactions involved in the alkaline treatment of oxycellulose at high temperature (auto-oxidation, peeling, stopping, alkaline degradation, hydrolysis of the compounds (I) to (III) of Figure 1), the method of Hofreiter et al. requires specified and carefully controlled conditions. It is likely that the analogy of mechanism between the β-alkoxy and peeling reactions led in the past some authors to hypothesise that β-alkoxy requires a hot alkaline treatment, as peeling does. Nevertheless, we have already shown that the β-alkoxy fragmentation is a fast reaction even at room temperature (Calvini et al. 2004) and the FTIR analysis (Calvini et al. 2006) showed that the reaction is practically complete within 24 h of alkaline treatment. In order to verify the application of the method without heating the

Table 1. Random (side) scissions calculated from the viscometric DPhmw of the high molecular weight fraction of oxidised samples (Equation 2).

Periodate oxidation time (h)	DPox	% loss[a]	DPhmw	Side scissions[b] from DPhmw
0	1216	0	1216	0.0
1	403	2	411	2.0
24	170	27	233	4.3
48	145	37	230	4.4
120	107	52	223	4.5
264	58	73	215	4.7

[a] As determined in a separate experiment through 24 h of treatment with 0.01 M NaOH.

[b] mmol/100 g, calculated from 617×(2/DPhmw −2/DP°).

oxycellulose samples, we decided to perform the titrimetric analysis at room temperature (Pommerening et al. 1992), after controlling the occurrence of the Cannizzaro's reaction. To this end, the soluble fraction of the 24 h oxidised sample subjected to alkaline treatment (2 h NaOH 0.01 M) was partly precipitated by reducing the pH to about 8, recovered and allowed to dry at room temperature. The FTIR analysis of the reddish/yellowish gummy residue showed all the characteristics of the carboxylate groups at about $1602\ \text{cm}^{-1}$, with the expected shift to about $1715\ \text{cm}^{-1}$ after further HCl treatment to restore the COOH function (Zhbankov 1966). These findings are in full agreement with the results of O'Meara and Richards (1958), who stated that both β-alkoxy fragmentation and Cannizzaro's reaction occur in moderate alkaline medium (even lime water) at room temperature.

The kinetics of β-alkoxy fragmentation was then evaluated by titrimetric analysis of the periodate oxidised samples left in 0.01 M NaOH for 0, 0.5, 1, 4 and 24 h at room temperature. It appeared that the 0.5 h of NaOH treatment was insufficient for the completeness of the β-alkoxy fragmentation of highly oxidised cellulose (264 h of periodate oxidation), while after 4 h (and even more after 24 h) of immersion in alkali the kinetic plots showed the same pattern obtained by Hofreiter et al. (1955) at 70 °C, with the occurrence of a secondary alkali-consuming reaction. The soluble fraction of the 24 h oxidised sample, left 1 month in the reaction vessel showed about 600% of alkali consumption, thus suggesting that the secondary reaction consists in the complete degradation of the glucose units. The results of the kinetic analyses allowed us to state that 1–2 h of treatment with 0.01 M NaOH at room temperature represents the best compromise between the required completeness of the β-alkoxy fragmentation and the minimisation of unwanted secondary reactions.

Table 2 shows the amount of NaOH consumption of samples subjected to increasing periodate oxidation, from which the percent of dialdehyde groups can be calculated. In order to compare the results of titrimetric analysis performed in alkaline medium with those obtained in a different way in acid medium, Table 2 shows also the percent of dialdehyde groups as determined by the hydroxylamine method. The latter values appear slightly lower at high degree of oxidation, possibly because of either an incomplete oximation (Maekawa and Koshijima 1991) or a diffusion limited reaction. A more precise analysis is beyond the limits of this work, but this finding should be further investigated taking also into account the persistence in acid medium of the FTIR band at about $880\ \text{cm}^{-1}$ (Calvini et al. 2006) generally assigned to the formation of hemiacetal bonds.

Table 2. NaOH consumption (mmol/100 g) due to oxidised units produced during the periodate oxidation.

Time of oxidation (h)	mmol/100 g	DAU %[a]	DAU %[b]
0	0	0	0.0
1	12.7	2.1	1.6
24	114	18.5	21.9
48	173	28.0	27.8
120	230	37.3	32.2
264	282	45.7	38.0

[a] Dialdehyde groups per 100 glucose units, as calculated from NaOH consumption.

[b] Dialdehyde groups per 100 glucose units, as calculated from hydroxylamine method.

By comparing the results of titrimetric (Table 2) with those of viscometric analyses (Table 1), it appears that the overall amount of dialdehyde groups was considerably higher than that of side groups alone even at low degree of oxidation, where some amorphous links remained still untouched and available (12.7 and 2.0 mmol/100 g respectively after 1 h of periodate treatment, with DPhmw ~2 times the levelling-off DP). This result suggests that periodate shows a great tendency to oxidise the cellulose chains in isolated domains (Kim et al. 2000), and led us to analyse the kinetics of overall periodate oxidation, as determined by titrimetric analysis, in order to shed some light on the mechanism of the reaction in spite of the fact that some data at high degrees of oxidation were lacking.

Kinetics of periodate oxidation

It is known (Veelaert et al. 1994) that periodate oxidation initially follows a second order kinetics, but later on the experimental data deviate from the kinetic model. In order to ascertain whether the deviation is due to two or more simultaneously occurring reactions (Tiziani et al. 2003), the second order kinetic parameters have been calculated with a spreadsheet following the method of Sihtola

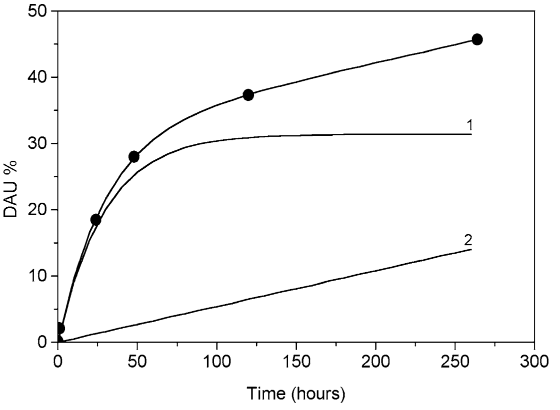

Figure 3. Amount of dialdehyde groups per 100 glucose residues produced during the time course of periodate oxidation, as determined by NaOH consumption. The overall kinetics (circles and line) is the sum of a fast (1) and a slow (2) reactions.

et al. (1963). However, the results obtained from titrimetric analysis (Table 2) can be fitted equally well with two pseudo first-order kinetics, whose parameters can be determined following Sharples (1954), as shown in Figure 3. Both the proposed algorithms require an estimation of the asymptotic limit of oxidation, taken here as 98% (Varma and Chavan 1995; Kim and Kuga 2001) and Table 3 gathers the obtained results.

It is worth noting that the sum of the asymptotic limits ($A_1 + A_2$) in the analysis of the second order kinetics does not reach the value of 98% and leaves behind a 0.1% of dialdehyde units, arising from an initial very fast oxidation (Painter and Larsen 1970), that should correspond (within the limits of the approximate algorithm utilised) to the amount already detected by the viscometric analysis.

Both the second- and the pseudo first-order analysis of the NaOH consumption show that the faster reaction of periodate oxidation introduces about 30 dialdehyde groups per 100 glucose units (A_1), while the large amount of oxidised groups (A_2) is due to a further, very slow oxidation. The pseudo first-order kinetic analysis gives respectively a half time of $t^{0.5} = 20$ h for the faster and $t^{0.5} = 854$ h (36 days) for the slower oxidation, and the attribution of these results to the mechanism of cellulose oxidation will be discussed later.

Table 3. Kinetic parameters of periodate oxidation, as determined by NaOH consumption.

	A_1 (fast)[a]	k_1 (fast)[b]	A_2 (slow)[a]	k_2 (slow)[b]
Second order	31.4%	2.2 E-4	66.5%	6.0 E-6
Pseudo first-order	31.4%	3.4 E-2	66.6%	8.1 E-4

[a] Asymptotic limits (% of oxidised cellulose units).
[b] Time-scale in h^{-1}.

Hydrolytic scissions

As stated in our previous article (Calvini et al. 2004), the amount of hydrolytic scissions induced by the acidity of periodate can be calculated by determining the viscometric DP of the oxidised samples subjected to reduction (dialcohol cellulose). To this end, Table 4 shows the values of DP obtained, respectively, from the oxidised cellulose after reduction with tert-buthylamino borane (DPoxred) and from never oxidised cellulose left in an acidic solution at the same pH ~4.5 of the periodate solution (DPac).

In spite of the fact that the reduction step was carried out at neutral pH, the amount of hydrolytic scissions calculated from the DPoxred after reduction is considerably higher than that of never oxidised cellulose left in acidic medium. Since the low molecular weight fragments have been washed

Table 4. Hydrolytic side scissions (mmol/100 g) calculated from the degree of polymerisation of oxidised and reduced samples (DPoxred), compared with those of never oxidised cellulose left at pH 4.5 (DPac).

Time of reaction[a] (h)	DPoxred	DPac	Scissions from DPoxred	Scissions from DPac
0	1216	1216	0.00	0.00
1	916	1215	0.33	0.00
24	567	1190	1.16	0.02
48	546	1165	1.25	0.04
120	426	1097	1.88	0.11
264	248	984	3.96	0.24

[a] Corresponding, respectively, to the time course of periodate oxidation for the DPoxred of the oxidised and reduced samples and to the time of permanence in acidic solution for the DPac of never oxidised cellulose.

away at the end of the reduction step, this anomalous behaviour can not be ascribed to the accumulation of oligomers (Calvini 2005). Without more specific analyses it is impossible to state whether the obtained results, that did not fully recover the initial DP of the never oxidised sample, are due to the sensitivity of oxidised groups to the acidity of periodate (Sihtola 1960; Maekawa and Koshijima 1991), to a still incomplete reduction or to the lower rigidity in the cupriethylenediamine solvent of the C2–C3 dialcohol cellulose chains, that might result in an increased fluidity (Sihtola 1960). In any case, a comparison with the titrimetric data indicates that the true hydrolytic scissions, not involving the oxidised units of cellulose, are negligible.

Conclusions

The kinetic analysis of periodate oxidation shows the occurrence of at least three simultaneously occurring reactions. A random oxidation, determined by viscometric analyses, proceeds at very high rate ($t^{0.5} = 1.2$ h), with a low asymptotic value (~0.7%) corresponding to the levelling-off degree of polymerisation. In the meanwhile, a second slow reaction ($t^{0.5} = 20$ h) occurs, generally attributed to the oxidation of the surface of crystallites, with an asymptotic limit corresponding to about 30% of oxidised anhydroglucose units, while a very slow third reaction ($t^{0.5} = 854$ h), possibly due to the oxidation of the crystalline core, leads to the asymptotic complete oxidation of the anhydroglucose units. The random initial oxidation occurs in the amorphous region of cellulose, while both the slower reactions contribute to the decrease of X-ray crystallinity (Rowland and Cousins 1966).

Nevertheless, this simple model is contradicted by the finding that even in the case of the most oxidised sample (264 h), whose overall oxidation was about 40%, we obtained a fibrous structure (Aimin et al. 2005) that, subjected to alkaline degradation, led to an insoluble residue with relatively high values of DP rather than to the expected narrow distribution of oligomers. It should be then postulated that all the above mechanisms take place in a highly heterogeneous way, as suggested by Kim et al. (2000), through a cooperative preferential oxidation of the neighbours of the already oxidised sites, similar to the 'quantum mode' acidic degradation of cellulose (Calvini 2005).

At first sight, this hypothesis does not explain the occurrence of the two slower reactions detected by titrimetry, but a possible interpretation can be drawn from the values of the weight loss, roughly corresponding to twice the amount of oxidised units. This finding suggests that an oxidised unit of cellulose might protect the corresponding hydroxyl groups of an adjacent cellulose chain by a transient hemiacetal/acetal structure in equilibrium with the free-aldehyde form (Painter and Larsen 1970; Ishak and Painter 1971; Guthrie 1975; Veelaert et al. 1994). Up to about 30–40% of oxidation there are enough unoxidised couples of cellulose units to allow a relatively fast rate of oxidation, but thereafter the transient hemiacetal/acetal protection of the remaining C2–C3 hydroxyl groups might cause the observed kinetic decrease. Such a speculative hypothesis should be verified in a properly performed analysis, but if an oxidised unit has at least one corresponding unoxidised unit, the soluble residue after the β-alkoxy fragmentation should contains also some chopped, unoxidised units of cellulose that might account for the non-volatile fragments found by O'Meara and Richards (1958). Moreover, in that case the latest very slow reaction (A2 and k2 in Table 3) might not follow the simple exponential kinetics assumed in this work, as suggested by the S-shaped results of Varma and Kulkarni (2002), so that some words of caution should be spent about the long-range extrapolation of the kinetic analysis in absence of experimental data.

It is worth noting that the fast initial attack of periodate introduces few dialdehyde units in cellulose, but their random displacement and perhaps some hydrolytic scissions strongly impairs the mechanical properties of the fibres, that thereafter slowly decrease and finally drop to very low values at increasing degrees of oxidation (Princi et al. 2004), until nothing but some unreacted crystallites (Calvini et al. 2006) should remain, embedded in a largely oxidised structure (Varma et al. 1997; Chavan et al. 2002).

Although the overall oxidation half time of our kinetic data is in good accordance with that of the plotted data of Kim et al. (2000), our value of oxidised units after 264 h of oxidation is about 40% lower, a difference that can be partly attributed to the different crystallinity of the reference paper samples. Nevertheless, some literature findings (Aimin et al. 2005) clearly indicate that the rate of periodate oxidation is very sensitive to the supramolecular structure of cellulose, so that the kinetic parameters detected in this work can not be generalised and should be taken as an useful tool to elucidate the mechanism of periodate oxidation.

Our results emphasise that simple analyses identify a cluster mechanism in the periodate oxidation, and the methodology utilised in this work can be utilised to cast further light on the topochemistry of other methods of cellulose oxidation. In particular, the sequence of analyses over the same sample (titrimetry, weight loss and viscometry), performed in mild conditions makes it possible to investigate the degree of oxidation of paper and textiles of historic and artistic value with microdistructive techniques on a single, very small fragment of material.

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